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Reaction of Diphenylphosphanylacetylene with $RB(C_6F_5)_2$ Reagents: Evidence for a Remarkable Sequence of Synergistic Frustrated *Lewis* Pair Addition Reactions

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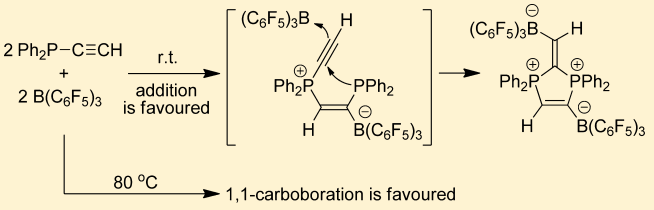
Supporting Information

ABSTRACT: Diphenylphosphanylethyne (**3a**) reacts with tris(pentafluorophenyl)borane at room temperature by a typical frustrated *Lewis* pair (FLP) reaction. It undergoes a sequential series of 1,2-phosphane/borane additions to the alkyne unit in an overall 2:2 molar ratio to selectively form the dimeric product **5a**. Product **5** features a pentafulvene-reminiscent structure with a pair of phosphonium units in the ring and $B(C_6F_5)_3$ substituents at the periphery. At elevated temperature, the reaction becomes less selective, now favoring the formation of cis- and trans-1,1-carboboration products from a 1:1 stoichiometry. After photolytic trans/cis isomerization, the vicinal FLP **6a** becomes the major product, featuring an intramolecular P···B interaction. The reaction of **3a** with $H_3CB(C_6F_5)_2$ also gives a heterocyclic dimer (**11**), except that here a substituent H/CH_3 exchange by an addition/elimination pathway has taken place. In the $B(C_6F_5)_3$-derived system, we were able to trap an alleged intermediate of this rearrangement reaction by adding *n*-butyl isocyanide. Five products in the Ph_2P- and $(p\text{-tolyl})_2P$-derived systems were characterized by X-ray diffraction



INTRODUCTION

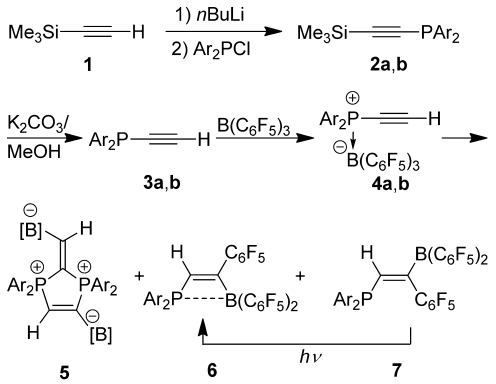
Phosphane/borane (P/B) frustrated *Lewis* pairs (FLPs)[1] can react with terminal acetylenes either by deprotonation, followed by alkynyl anion addition, e.g., to the borane *Lewis* acid,[2] or by synergistic 1,2-addition of the P/B pair to the C≡C triple bond.[3] Alternatively, strongly electrophilic $RB(C_6F_5)_2$ boranes undergo 1,1-carboboration reactions[4−6] with various alkynes, especially when good migrating groups are present at the acetylenic substrate, such as, e.g., PR_2,[7,8] SiR_3,[9] SR,[10] and even H.[5,6] This may pose a serious selectivity problem when singly phosphanyl-substituted alkynes, such as, e.g., $Ph_2PC{\equiv}CH$ (**3a**), are treated with the $RB(C_6F_5)_2$ reagents. Principally, one might envisage that this would be a typical case of 1,1-carboboration with facile internal phosphanyl migration. However, the **3a**/$RB(C_6F_5)_2$ combination itself may constitute a P/B FLP that might be able to add to another acetylene unit in the typical FLP way. We investigated some such systems and found a remarkable array of competing reaction pathways being followed depending on the specific reaction conditions applied.

RESULTS AND DISCUSSION

The diarylphosphanylacetylenes **3a** (Ar = phenyl) and **3b** (Ar = *p*-tolyl) were prepared in a two-step process by the treatment of lithiated (trimethylsilyl)acetylene (**1**) with the respective Ar_2PCl reagents followed by deprotection.[11]

The treatment of **3a** with 1 molar equiv of the strong boron *Lewis* acid $B(C_6F_5)_3$ was first carried out under direct NMR observation in a deuterated solvent (toluene-d_8). We observed the formation of the adduct **4a** at low temperature (−60 °C;[12] see Scheme 1). This was not isolated, but it was characterized by, e.g., a ^{31}P NMR signal at δ 4.3, a ^{11}B NMR resonance at δ −8.8, and an acetylene CH ^1H NMR resonance at δ 1.54 (1H, $^3J_{PH}$ = 8.9 Hz).

Scheme 1



		5	6	7
a (Ar = Ph)	r.t. (1h)	>99	-	-
	80 °C (1h)	39	26	31
	then *hν*	41	54	-
b (Ar = *p*-tol)	r.t. (7d)	57	16	3
	80 °C (1h)	26	32	27
	then *hν*	28	56	-

in mol%

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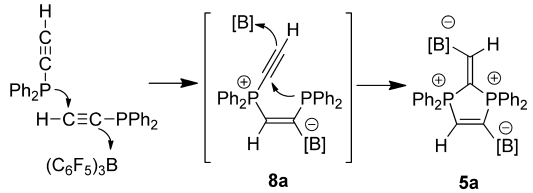
The reaction of **3a** with $B(C_6F_5)_3$ was then carried out on a preparative scale and found to proceed smoothly to the product **5a** in a toluene solution (1 h, room temperature). Workup involving precipitation from dichloromethane at −30 °C eventually gave compound **5a** as a white solid, which was isolated in ca. 60% yield (see Scheme 1).

In solution (CD_2Cl_2), compound **5a** features pairs of clearly separated ^{11}B (δ −13.1 and −15.1) and ^{31}P NMR (δ 53.8 and 15.5, $^2J_{PP} \approx 145$ Hz) signals. They are located in the typical borate and phosphonium chemical shift range. The olefinic ^1H NMR ([B]C4)H (see Figure 2 for the numbering scheme) resonance occurs as a dd at δ 9.40 ($^3J_{PH}$ = 53.7 and 31.3 Hz), and the corresponding endocyclic (C3)H signal is at δ 7.37 (dd, $^3J_{PH}$ = 53.2 Hz, $^2J_{PH}$ = 28.6 Hz). The ^{13}C NMR signals of the exocyclic C═C double bond were located at δ 210.9 [([B]C4)H] and 107.9 (C1, $^1J_{PC}$ = 86.7 Hz, $^1J_{PC}$ = 66.4 Hz), respectively. The corresponding ^{13}C NMR signals of the endocyclic C═C bond were found at δ 138.7 [(C3)H, $^1J_{PC}$ = 79.6 Hz] and 167.7 (C2, br), respectively.

We assume that product **5a** was formed in a typical sequence of 1,2-P/B FLP addition reactions[3] to the C≡C triple bonds of a pair of the starting material **3a** (see Scheme 2). Probably, **3a**

Scheme 2



forms a reactive FLP (in equilibrium with their *Lewis* acid/*Lewis* base adduct) with $B(C_6F_5)_3$ that is able to add to the C≡C triple bond of another **3a** molecule to form the intermediate **8a**. This can then itself react with an external $B(C_6F_5)_3$ *Lewis* acid by FLP addition to the remaining C≡C triple bond of **8a** to directly yield the observed dimeric product **5a**.

The reaction is markedly less selective at elevated temperature. The reaction between **3a** and $B(C_6F_5)_3$ in toluene at 80 °C (1 h) gives a mixture of three products in a ca. 39:26:31 ratio. One product is the cyclic dimer **5a**, which was formed by a typical FLP reaction sequence; the two new products are both probably arising from competing 1,1-carboboration reactions. One product was identified as the cyclic P/B FLP **6a** (see below). To the other we tentatively ascribed the structure of its respective trans isomer **7a** (see Scheme 1). This would be in accordance with the observation that 1,1-carboboration reactions often proceed stereounselectively to give cis/trans product mixtures.[6] In addition, we photolyzed the reaction mixture and found that compound **7a** was cleanly isomerized to **6a**. After ca. 3 h of irradiation, the original 39:26:31 mixture of products **5a**, **6a**, and **7a** had changed to a ca. 41:54 mixture of **5a** and **6a**. The ratios were determined from ^{31}P NMR spectra from an in situ experiment (for details, see the Supporting Information). From a stepwise workup procedure, we eventually isolated the 1,1-carboboration product **6a** as a white solid in ca. 12% yield.

The X-ray crystal structure analysis of compound **6a** (single crystals were obtained from the slow diffusion of pentane into a saturated CH_2Cl_2 solution at −30 °C) shows the typical pattern of a product formed by 1,1-carboboration (see Figure 1).

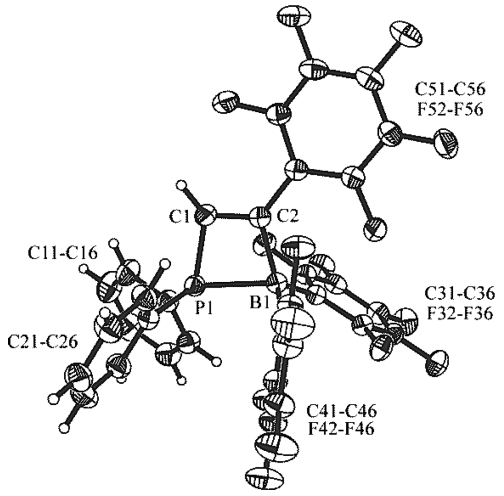


Figure 1. Molecular structure of the 1,1-carboboration product **6a** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å), angles (deg), and dihedral angles (deg): C1−C2 1.348(3), C1−P1 1.775(2), C2−B1 1.651(3), B1−P1 2.045(2); C1−P1−B1 77.1(1), C2−B1−P1 79.4(1), P1−C1−C2 98.4(1), C1−C2−B1 105.2(2); P1−C1−C2−B1 −1.(2), C1−C2−B1−P1 0.9(1).

The borane has added to an acetylenic carbon atom and induced 1,2-migration of the PPh_2 substituent concomitant with 1,2-migration of a C_6F_5 substituent from boron to carbon. The resulting olefinic product **6a** consequently contains a geminal pair of C_6F_5 and $B(C_6F_5)_2$ substituents at one former acetylene carbon and a H/PPh_2 pair at the other. In the isolated isomer, the phosphanyl and boryl substituents were found to be cis to each other. They show a direct P···B interaction, as is typical of unsaturated vicinal P/B FLPs of this type.[7]

The reaction of (p-tolyl)$_2$PC≡CH (**3b**) with $B(C_6F_5)_3$ takes a similar course. We first observed P/B adduct formation at ca. −60 °C [**4b**: δ −9.9 (^{11}B NMR), 4.1 (^{31}P NMR)]. In contrast to the Ph_2P-substituted system **4a**, the $B(C_6F_5)_3$ adduct **4b** is much more thermally robust. It required prolonged stirring at ambient temperature to be consumed. In this case, the formation of the follow-up products is much less selective (for details, see the Supporting Information). Prolonged stirring of the mixture (**4b**) at room temperature eventually resulted in formation of the dimeric FLP addition product **5b** admixed with the 1,1-carboboration products **6b** and **7b** and an additional not yet unequivocally identified fourth product. Workup eventually gave the coupling product **5b** in 52% yield as a white solid.

Compound **5b** was characterized by X-ray diffraction (single crystals were obtained by keeping a saturated CH_2Cl_2 solution at room temperature for several days). Structure determination showed that the product was produced from the reaction of 2 mol equiv of each **3b** and $B(C_6F_5)_3$. The resulting cyclodimer features a central five-membered heterocycle that contains a pair of Ar_2P units. All of the endocyclic carbon atoms are sp^2-hybridized. A $B(C_6F_5)_3$ substituent is found bonded to carbon atom C2 of the endocyclic C═C double bond. Carbon atom C1 is part of an exocyclic C═C double bond, to the end of which (C4) the second $B(C_6F_5)_3$ substituent is bonded (see Figure 2).

Heating of the **3b**/$B(C_6F_5)_3$ reaction mixture for 1 h at 80 °C gave a ca. 26:32:27 mixture of the products **5b**, **6b**, and **7b** (see Scheme 1; for details, see the Supporting Information). Compound **7b** again was tentatively assigned by its NMR spectra from the mixture. After removal of the product **5b**, the filtrate was photolyzed for 3 h, and eventually we isolated the 1,1-carboboration

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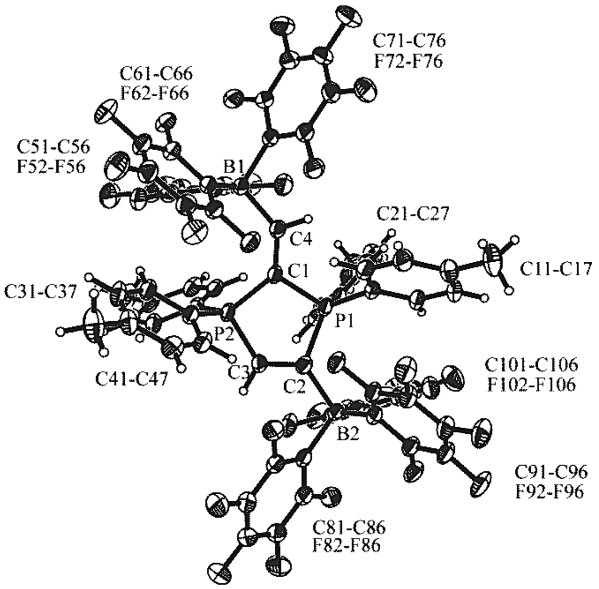

Figure 2. Molecular structure of compound **5b** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (deg): C1−P2 1.785(4), P2−C3 1.783(4), C3−C2 1.325(5), C2−P1 1.839(4), C1−P1 1.813(4), C1−C4 1.353(5), C2−B2 1.681(5), C4−B1 1.654(5); C1−P2−C3 97.4(2), C1−P1−C2 100.9(2), C1−C4−B1 135.7(3), C2−B2−C81 110.4(3), P1−C1−P2 107.9(2).

product **6b** in ca. 19% yield. It was characterized by X-ray diffraction (see Figure 3) and shown to represent an example of an FLP with a reasonably strong P···B interaction.

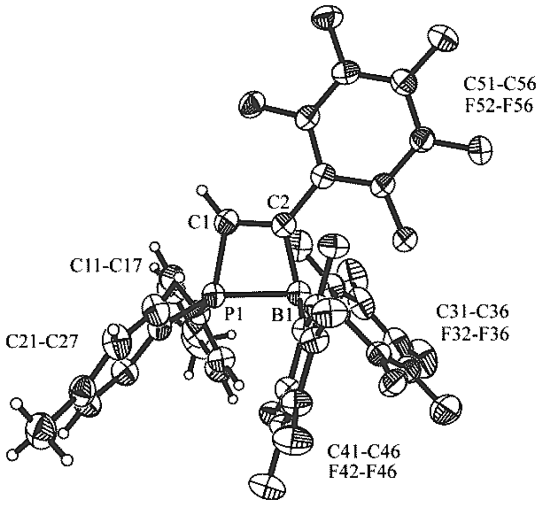

Figure 3. Molecular structure of the FLP **6b** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å), angles (deg), and dihedral angles (deg): C1−C2 1.359(4), C1−P1 1.770(3), C2−B1 1.627(4), B1−P1 2.057(3); C1−P1−B1 76.4(1), C2−B1−P1 79.8(2), P1−C1−C2 98.6(2), C1−C2−B1 105.1(2); P1−C1−C2−B1 −2.7(2), C1−C2−B1−P1 2.3(2).

Compound **6b** shows the typical NMR features of the C═C unsaturated FLP system, namely, heteronuclei NMR resonances at δ −4.7 (^{11}B NMR) and 12.0 (^{31}P NMR), respectively. It shows the ^{19}F NMR signals of the pair of C_6F_5 substituents at boron at δ −131.3, −158.2, and −165.2 [$\Delta^{19}F_{m,p}$ = 7.0] and the corresponding signals of the migrated C_6F_5 group at δ −137.8, −153.1, and −163.6 [$\Delta^{19}F_{m,p}$= 10.5]. The ^{1}H NMR resonance of the single ═CH− group at the bridge was located at δ 7.29 ($^2J_{PH}$ = 12.9 Hz) with corresponding ^{13}C NMR signals at δ 126.5 (═C−, $^1J_{PC}$ = 58.5 Hz) and 170.2 (═C[B], br), respectively.

We then reacted diphenylphosphanylacetylene **3a** with 1 mol equiv of the borane $H_3CB(C_6F_5)_2$.[13] The reaction took 5 h at 80 °C. The product was identified by X-ray crystal structure analysis as the dimeric hetercyclic derivative **11** (see Figure 4). Compound

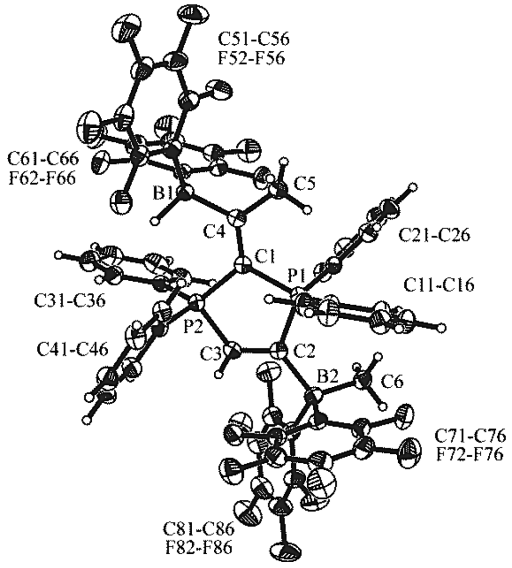

Figure 4. View of the molecular structure of compound **11** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (deg): C1−P1 1.802(3), P1−C2 1.814(3), C2−C3 1.340(4), P2−C3 1.791(3), P2−C1 1.783(2), C1−C4 1.359(3), B1−C4 1.631(4), B2−C2 1.653(4), B2−C6 1.629(4); C1−P2−C3 98.0(1), C1−P1−C2 101.4(1), C1−C4−B1 120.5(2), B1−C4−C5 119.0(2), C2−B2−C6 112.3(2), C2−B2−C81 111.6(2).

11 has a framework analogous to that already found for compound **5b** (see above), but it bears a slightly, but nevertheless, distinctly different substituent pattern. For **11**, we have found a five-membered heterocyclic core structure that contains the pair of phosphonium units that is typical for this type of an "FLP dimer". It features the $B(C_6F_5)_2CH_3$ substituent at the endocyclic sp^2-hybridized carbon atom C2 and an exocyclic C═C double bond attached at carbon atom C1. The adjacent carbon atom C4, however, has a CH_3 group bonded to it and, consequently, it also bears a $B(H)(C_6F_5)_2$ substituent. In the end, we have found a situation where at this end of the dimer a CH_3 substituent and an H substituent have exchanged their expected positions.

This specific composition of compound **11** has been confirmed in solution (CD_2Cl_2) by its NMR spectra. It shows the typical pair of ^{31}P NMR resonances [δ 33.1 and 22.2 ($^2J_{PP}$ ~ 158 Hz)] and the $B(C_6F_5)_2CH_3$ ^{11}B NMR resonance at δ −11.9. The second ^{11}B NMR resonance occurs at δ −15.9; it is split into a doublet due to the bonded hydride ($^1J_{BH}$ ~ 88 Hz). The corresponding [B]H ^{1}H NMR resonance was located as a partially relaxed broadened 1:1:1:1 quartet at δ 3.36. The methyl group that was shifted from boron to the adjacent carbon atom (C4) during the reaction gives rise to a ^{1}H NMR signal at δ 2.16 (corresponding ^{13}C NMR resonance at δ 31.3). The ^{13}C NMR signals of the exocyclic C═C double bond occur at δ 226.7 (═C[CH_3][B]) and δ 101.5 ($^1J_{PC}$ = 95.5 and 67.0 Hz), respectively. The endocyclic C═C double bond gives rise to

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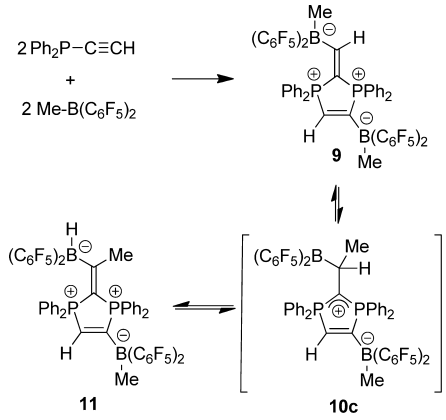
NMR features at δ 140.0 [$^1J_{PC}$ = 75.1 Hz, =C–, corresponding ^{1}H NMR resonance at δ 7.31 (J_{PH} = 52.4 and 29.0 Hz)] and 173.0 (br), respectively.

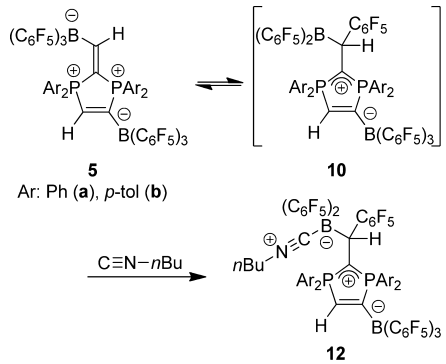
The formation of compound **11** in the reaction between **3a** and $H_3CB(C_6F_5)_2$ indicates that there has been a H/CH_3 exchange reaction taking place along the reaction pathway involving the "normal" dimer **9** (for details, see the Supporting Information). We assume that the geminal pair of phosphonium substituents makes the terminus of the adjacent exocyclic C=C double bond sufficiently electrophilic that it becomes amenable to nucleophilic methyl attack from the adjacent borate anion. This would lead to the intermediate **10c**. Subsequent 1,2-hydride migration to boron would represent a viable possibility to explain the formation of the observed and isolated product **11** (see Scheme 3).

Scheme 3



This view has been supported by the outcome of a trapping reaction starting from the heterocycle **5a**. Stirring compound **5a** for 10 min with 1 equiv of *n*-butyl isocyanide in a dichloromethane solution at room temperature led to formation of the isonitrile/borane adduct **12a**, which was isolated in 83% yield after workup (see Scheme 4). The product was characterized by

Scheme 4



carbon, hydrogen, and nitrogen elemental analysis, spectroscopy, and X-ray diffraction (single crystals were obtained from the slow diffusion of pentane into a saturated CH_2Cl_2 solution at −30 °C).

The crystal structure analysis has revealed that compound **12a** contains the intact unsaturated five-membered heterocyclic core (see Figure 5). The $B(C_6F_5)_3$ substituent is bonded to its endocyclic C=C double bond. The "tip" of the five-membered heterocycle is made up of a single sp^2-hybridized carbon atom (C1). Formally, it is part of an ylidic structure,[14] but it features

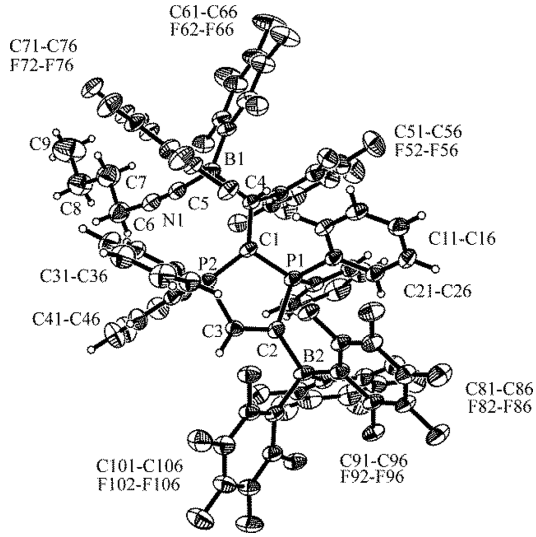


Figure 5. Molecular structure of compound **12a** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (deg): C2–P1 1.832(5), P1–C1 1.736(4), C2–C3 1.336(6), C3–P2 1.786(4), P2–C1 1.714(5), C1–C4 1.573(6), C2–B2 1.656(6), C4–B1 1.667(6), C5–B1 1.623(9); C3–P2–C1 99.9(2), C1–P1–C2 104.3(2), C1–C4–B1 124.5(4), C4–B1–C5 111.2(4), B1–C5–N1 172.8(5), P1–C1–P2 108.0(2).

delocalization over both phosphorus atoms.[15] The sp^3-hybridized carbon atom C4 is bonded to it. Carbon atom C4 is four-coordinated, having C_6F_5, H, and boryl substituents. The $B(C_6F_5)_2$ group has formed an adduct with the added *n*-butyl isocyanide donor.

So, it seems that in this reaction the isonitrile has trapped the free borane *Lewis* acid of an isomer of **5a**, namely, of the reactive intermediate **10a** that was formed (in an equilibrium situation) with **5a** by a 1,2-C_6F_5 shift from boron to carbon. This is the analogous reaction that has been proposed for the formation of the substituent exchange product **11** (see Scheme 3), except in this case a C_6F_5 group has migrated (see Scheme 4).

Compound **12a** shows an AX pattern of ^{31}P NMR resonances at δ 56.3 and 22.3 ($^2J_{PP}$ ~ 150 Hz). It shows two ^{11}B NMR signals (δ −13.5 and −17.9). The isonitrile sp-hybridized carbon resonance of compound **12a** occurs at δ 127.7. The ^{13}C NMR resonances of the −CH[B]C_6F_5 substituent (C4) was found at δ 20.4 (br, ^{1}H NMR δ 4.73); the adjacent "ylidic" carbon (C1) shows a ^{13}C NMR signal at δ 15.6 ($^1J_{PC}$ ~ 118 and 90 Hz). The corresponding ^{13}C signals of the endocyclic C=C unit were located at δ 162.1 (=C[B], br) and 140.8 (=C–, $^1J_{PC}$ = 86.3 Hz); ^{1}H NMR δ 6.80 (J_{PH} = 55.8 and 33.1 Hz), respectively.

CONCLUSIONS

P/B FLPs are known to react with terminal alkynes. Either they can undergo an acid–base reaction, yielding a phosphonium/alkynylborate salt, or they can simply add 1,2 to the C≡C triple bond. Alternatively, alkynes can undergo 1,1-carboboration reactions just with the borane component of the FLP alone without involving the phosphane at all.

The here-employed **3a**/borane system represents an interesting hybrid between these principal reaction alternatives. The substrate **3a** contains both a phosphane and an alkyne functional group. Therefore, it can undergo a 1,1-carboboration reaction, probably proceeding with PPh_2 migration, to give a 1-phosphanyl-2-borylalkene product. At least in its cis isomer, the phosphane

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component of this newly formed vicinal FLP is involved, because in the product **6a**, it features a P···B interaction.

However, this attractive reaction pathway has only been observed at high reaction temperature, and then the 1,1-carboboration reaction (to give **6a** and **7a**) is only a competing reaction with 1,2-P/B FLP addition. The reaction becomes quite selective in favor of the FLP addition reaction alternative at room temperature. Here we have found formation of the five-membered heterocyclic "dimeric" product **5a** (and, consequently, also **5b**) to prevail under these milder reaction conditions. Even in the case of the **3a**/$H_3CB(C_6F_5)_2$ reaction, this pathway seems to be favored, although it is followed in this specific case by a subsequent rearrangement reaction.

We conclude that we have found a unique reaction system where the bifunctional alkyne **3a** reacts very selectively with a strongly electrophilic borane by a typical FLP reaction pathway to yield the interesting 2-fold P/B alkyne addition product **5a**. The 1,1-carboboration pathway, which is always an alternative, is in this case only observed as a competing reaction at elevated temperature, i.e., in a regime where the **3** + $B(C_6F_5)_3$ reaction system has become quite unselective. These observations may help us and others to determine reaction conditions for selective FLP reactions without accompanying reaction alternatives becoming too dominant.

EXPERIMENTAL SECTION

General Procedures. Standard Schlenk-type glassware (or glovebox) under an atmosphere of argon was used in the syntheses involving air- and/or moisture-sensitive compounds. Solvents were dried, and X-ray crystal structure analyses were performed. Data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, *COLLECT*;[16] data reduction, *Denzo-SMN*;[17] absorption correction, *Denzo*;[18] structure solution, *SHELXS-97*;[19] structure refinement, *SHELXL-97*;[20] graphics, *XP* (BrukerAXS, 2000). Thermal ellipsoids are shown with 30% probability, *R* values are given for observed reflections, and wR2 values are given for all reflections. Exceptions and special features: Two disordered over two position dichloromethane molecules were found in the asymmetric unit of compound **5b**. Several restraints (SAMI, SAME, ISOR, and SADI) were used in order to improve the refinement stability. Compound **6a** crystallized with one disordered over two position toluene molecules in the asymmetric unit. Several restraints (SAMI, SAME, ISOR, and SADI) were used in order to improve the refinement stability. In compound **11**, the hydrogen at the B1 atom was refined freely. Compound **12a** contains an unidentified disordered solvent molecule in the asymmetrical unit, which could not be satisfactorily refined. The program *SQUEEZE*[21] was therefore used to mathematically remove the effect of the solvent. The quoted formula and derived parameters are not included in the squeezed solvent molecule.

Generation of Compound 4a (NMR Scale). Diphenylphosphanylethyne (11 mg, 50 μmol) and tris(pentafluorophenyl)borane (26 mg, 50 μmol) were mixed in toluene-d_8 (1.0 mL) at −78 °C in an NMR tube. Then the reaction mixture was directly measured by NMR experiments starting at −60 °C. ^{1}H NMR (600 MHz, 213 K, toluene-d_8): δ 7.29 (m, 4H, *o*-Ph), 6.66 (m, 2H, *p*-Ph), 6.49 (m, 4H, *m*-Ph), 1.54 (d, $^3J_{PH}$ = 8.9 Hz, 1H, ≡CH). ^{13}C{^{1}H} NMR (151 MHz): δ 148.7 (dm, $^1J_{FC} \approx$ 240 Hz, C_6F_5), 140.6 (dm, $^1J_{FC} \approx$ 255 Hz, C_6F_5), 137.2 (dm, $^1J_{FC} \approx$ 250 Hz, C_6F_5), 132.8 (*o*-Ph), 132.3 (*p*-Ph), 128.7 (*m*-Ph) [from the ghsqc experiment], 124.1 (d, $^1J_{PC}$ = 58.0 Hz, *i*-Ph), 114.9 (br, *i*-C_6F_5), 101.8 (dm, $^2J_{PC}$ = 9.9 Hz, ≡CH), 71.5 (dm, $^1J_{PC}$ = 107.8 Hz, ≡CP). ^{11}B{^{1}H} NMR (192 MHz): δ −8.8 ($\nu_{1/2} \approx$ 800 Hz). ^{31}P{^{1}H} NMR (243 MHz): δ 4.3 ($\nu_{1/2} \approx$ 40 Hz). ^{19}F NMR (564 MHz): δ −127.2 (br, 2F, *o*-C_6F_5), −155.3 (br, 1F, *p*-C_6F_5), −163.9 (br, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 8.6].

Generation of Compound 4b (NMR Scale). After di-*p*-tolylphosphanylethyne (12 mg, 50 μmol) and tris(pentafluorophenyl)borane (26 mg, 50 μmol) were mixed in toluene-d_8 (1.0 mL) at −78 °C in a NMR tube, the reaction mixture was measured by NMR experiments at −60 °C. ^{1}H NMR (600 MHz, 213 K, toluene-d_8): δ 7.28 (m, 4H, *o*-tolyl), 6.37 (m, 4H, *m*-tolyl), 1.64 (s, 3H, CH_3), 1.57 (d, $^2J_{PH}$ = 9.0 Hz, 1H, ≡CH). ^{13}C{^{1}H} NMR (151 MHz): δ 148.8 (dm, $^1J_{FC} \approx$ 240 Hz, C_6F_5), 143.2 (*p*-tolyl), 140.6 (dm, $^1J_{FC} \approx$ 250 Hz, C_6F_5), 137.3 (dm, $^1J_{FC} \approx$ 250 Hz, C_6F_5), 132.9 (d, $^2J_{PC}$ = 8.3 Hz, *o*-tolyl), 129.5 (d, $^3J_{PC}$ = 11.0 Hz, *m*-tolyl), 121.1 (d, $^1J_{PC}$ = 60.1 Hz, *i*-tolyl), 115.2 (br, *i*-C_6F_5), 101.0 (dm, $^2J_{PC} \approx$ 12 Hz, ≡CH), 72.2 (d, $^1J_{PC}$ = 108.0 Hz, ≡CP), 20.7 (CH_3). ^{11}B{^{1}H} NMR (192 MHz): δ −9.9 ($\nu_{1/2} \approx$ 700 Hz). ^{31}P{^{1}H} NMR (243 MHz): δ 4.1 ($\nu_{1/2} \approx$ 40 Hz). ^{19}F NMR (564 MHz): δ −127.1 (br, 2F, *o*-C_6F_5), −155.2 (br, 1F, *p*-C_6F_5), −163.7 (br, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 8.5].

Synthesis of Compound 5a. The mixing of diphenylphosphanylethyne (0.11 g, 0.50 mmol) with tris(pentafluorophenyl)borane (0.26 g, 0.50 mmol) in toluene (6 mL) at room temperature led to a light-brown solution. After 1 h of stirring, all volatiles were removed in vacuo. The obtained residue was dissolved in CH_2Cl_2 (1 mL). Then the solution was kept overnight at −30 °C. Subsequently, the white precipitate was isolated by cannula filtration and dried in vacuo to give the product (0.21 g, 0.15 mmol, 60%) as a white powder. Mp: 320 °C (dec). Elem anal. Calcd for $C_{64}H_{22}B_2F_{30}P_2$: C, 53.22; H, 1.54. Found: C, 52.94; H, 1.45. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ 9.40 (dd, $^3J_{PH}$ = 53.7 and 31.3 Hz, 1H, BCH), 7.85 (m, 2H, *p*-Ph^A), 7.77 (m, 2H, *p*-Ph^B), 7.58 (m, 4H, *m*-Ph^A), 7.56 (m, 4H, *o*-Ph^B), 7.51 (m, 4H, *m*-Ph^B), 7.47 (m, 4H, *o*-Ph^A), 7.37 (dd, $^3J_{PH}$ = 53.2 Hz, $^2J_{PH}$ = 28.6 Hz, 1H, PCH). ^{13}C{^{1}H} NMR (151 MHz): δ 210.9 (br m, BCH), 167.7 (br, BCP), 138.7 (d, $^1J_{PC}$ = 79.6 Hz, PCH), 136.3 (d, $^4J_{PC}$ = 3.1 Hz, *p*-Ph^A), 135.6 (d, $^4J_{PC}$ = 3.1 Hz, *p*-Ph^B), 134.0 (d, $^3J_{PC}$ = 10.1 Hz, *o*-Ph^B), 133.7 (d, $^3J_{PC}$ = 11.6 Hz, *o*-Ph^A), 130.5 (d, $^3J_{PC}$ = 13.5 Hz, *m*-Ph^A), 129.9 (d, $^3J_{PC}$ = 13.0 Hz, *m*-Ph^B), 118.3 (d, $^1J_{PC}$ = 83.0 Hz, *i*-Ph^B), 116.5 (d, $^1J_{PC}$ = 87.9 Hz, *i*-Ph^A), 107.9 (dd, $^1J_{PC}$ = 86.7, $^1J_{PC}$ = 66.4 Hz, PCP) (C_6F_5 not listed). ^{11}B{^{1}H} NMR (192 MHz): δ −13.1 ($\nu_{1/2} \approx$ 34 Hz), −15.1 ($\nu_{1/2} \approx$ 27 Hz). ^{31}P{^{1}H} NMR (243 MHz): δ 53.8 (d, $^2J_{PP} \approx$ 145 Hz), 15.5 (d, $^2J_{PP} \approx$ 145 Hz). ^{19}F NMR (564 MHz): δ −128.3, −130.3 (each br, each 2F, *o*-C_6F_5), −159.2 (t, $^3J_{FF}$ = 20.9 Hz), −159.3 (t, $^3J_{FF}$ = 20.9 Hz, each 1F, *p*-C_6F_5), −164.4 (m, 4F, *m*-C_6F_5) [$\Delta^{19}F_{m,p}$ = 5.2 and 5.1].

Synthesis of Compound 5b. Di-*p*-tolylphosphanylethyne (0.12 g, 0.50 mmol) and tris(pentafluorophenyl)borane (0.26 g, 0.50 mmol) were dissolved in toluene (2 mL) and stirred at room temperature for 7 days until the solution turned brown. Then all volatiles were removed in vacuo, and the obtained residue was washed with cold CH_2Cl_2 (2 × 0.5 mL). Drying of the solid in vacuo yielded **5b** (0.19 g, 0.13 mmol, 52%) as a white powder. Single crystals of **5b** suitable for X-ray single crystal structure analysis were obtained by keeping a saturated CH_2Cl_2 solution at room temperature for 1 week. Mp: 300 °C (dec). Elem anal. Calcd for $C_{68}H_{30}B_2F_{30}P_2$: C, 54.43; H, 2.02. Found: C, 54.62; H, 2.05. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ 9.28 (dd, $^3J_{PH}$ = 53.2 and 30.9 Hz, 1H, BCH), 7.43 (m, 4H, *o*-tolyl^A), 7.37 (m, 8H, *o*,*m*-tolyl^B), 7.31 (m, 4H, *m*-tolyl^A), 7.26 (dd, $^3J_{PH}$ = 54.0 Hz, $^2J_{PH}$ = 28.2 Hz, 1H, PCH), 2.52 (s, 6H, CH_3^B), 2.47 (s, 6H, CH_3^A). ^{13}C{^{1}H} NMR (151 MHz): δ 209.8 (br m, BCH), 167.3 (br, BCP), 148.4 (d, $^4J_{PC}$ = 3.2 Hz, *p*-tolyl^B), 147.4 (d, $^4J_{PC}$ = 3.1 Hz, *p*-tolyl^A), 138.3 (d, $^1J_{PC}$ = 80.0 Hz, PCH), 133.9 (d, $^2J_{PC}$ = 11.1 Hz, *o*-tolyl^A), 133.6 (d, $^2J_{PC}$ = 12.1 Hz, *o*-tolyl^B), 131.2 (d, $^3J_{PC}$ = 14.1 Hz, *m*-tolyl^B), 130.4 (d, $^3J_{PC}$ = 13.6 Hz, *m*-tolyl^A), 115.1 (d, $^1J_{PC}$ = 86.0 Hz, *i*-tolyl^A), 113.0 (dd, $^1J_{PC}$ = 90.5 Hz, *J* = 3.7 Hz, *i*-tolyl^B), 109.0 (dd, $^1J_{PC}$ = 86.9 and 67.0 Hz, PCP), 22.0 (d, $^5J_{PC}$ = 1.6 Hz, CH_3^B), 21.7 (d, $^5J_{PC}$ = 1.5 Hz, CH_3^A) [C_6F_5 not listed]. ^{11}B{^{1}H} NMR (192 MHz): δ −13.2 ($\nu_{1/2} \approx$ 35 Hz), −15.2 ($\nu_{1/2} \approx$ 30 Hz). ^{31}P{^{1}H} NMR (243 MHz): δ 53.0 (d, $^2J_{PP} \sim$ 146 Hz), 14.5 (d, $^2J_{PP} \sim$ 146 Hz). ^{19}F NMR (564 MHz): δ −128.4, −130.3 (each br, each 2F, *o*-C_6F_5), −159.7 (t, $^3J_{FF}$ = 20.1 Hz), −159.9 (t, $^3J_{FF}$ = 20.0 Hz, each 1F, *p*-C_6F_5), −164.8 (m, 4F, *m*-C_6F_5).

X-ray Crystal Structure Analysis of Compound 5b. Formula $C_{68}H_{30}B_2F_{30}P_2{\cdot}2CH_2Cl_2$, M = 1670.33, colorless crystal, 0.18 × 0.13 × 0.07 mm, a = 13.2281(7) Å, b = 13.9512(5) Å, c = 19.8440(11) Å, α = 86.049(5)°, β = 84.316(4)°, γ = 67.594(4)°, V = 3367.1(3) Å^3, ρ_{calc} = 1.647 g cm^{-3}, μ = 3.211 mm^{-1}, empirical absorption correction (0.595 ≤ T ≤ 0.806), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 46868 reflections collected (±h, ±k, ±l), (sin θ)/λ = 0.60 Å^{-1}, 11646 independent (R_{int} = 0.066) and 9492

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observed reflections [$I > 2\sigma(I)$], 1033 refined parameters, R1 = 0.074, wR2 = 0.205, max (min) residual electron density 0.83 (−0.53) e Å^{-3}. Hydrogen atoms were calculated and refined as riding atoms.

Synthesis of Compound 6a. Immediately after diphenylphosphanylethyne (84 mg, 0.40 mmol) and tris(pentafluorophenyl)borane (0.20 g, 0.40 mmol) were mixed in toluene (4.0 mL), the reaction mixture was heated for 1 h at 80 °C. Then the light-brown reaction mixture was concentrated to approximately one-third in vacuo and kept stirring at room temperature overnight. The obtained precipitate was collected by cannula filtration and dried in vacuo to give **5a** (60 mg, 42 μmol, 21%) as a white powder. The yellow filtrate was then irradiated under UV light (high-pressure mercury vapor lamp: HPK 125 W, Pyrex filter) for 3 h until the solution turned colorless. Subsequently, the solvent was removed in vacuo, and the residue was crystallized from a pentane solution to give **6a** (35 mg, 48 μmol, 12%) as a white powder. Single crystals of **6a** suitable for X-ray single crystal structure analysis were obtained by the slow diffusion of pentane into a saturated CH_2Cl_2 solution at −30 °C. Mp: 158 °C. Elem anal. Calcd for $C_{32}H_{11}BF_{15}P$: C, 53.22; H, 1.54. Found: C, 52.94; H, 1.45. ^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ 7.53 (m, 2H, *p*-Ph), 7.41 (m, 4H, *m*-Ph), 7.34 (d, $^2J_{PH}$ = 12.4 Hz, 1H, =CH) [from the ghsqc experiment], 7.33 (m, 4H, *o*-Ph). ^{13}C{^{1}H} NMR (126 MHz): δ 171.0 (br, =CB), 132.4 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Ph), 132.1 (d, $^2J_{PC}$ = 9.5 Hz, *o*-Ph), 129.5 (d, $^3J_{PC}$ = 11.6 Hz, *m*-Ph), 125.8 (dm, $^1J_{PC}$ = 58.1 Hz, =CH), 125.8 (d, $^1J_{PC}$ = 45.6 Hz, *i*-Ph) [C_6F_5 is not listed]. ^{11}B{^{1}H} NMR (160 MHz): δ −4.3. ^{31}P{^{1}H} NMR (202 MHz): δ 11.8 ($\nu_{1/2} \approx 80$ Hz). ^{19}F NMR (470 MHz): δ −137.6 (m, 2F, *o*), −152.8 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*), −163.4 (m, 2F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 10.6], −131.2 (m, 4F, *o*), −157.9 (t, $^3J_{FF}$ = 19.6 Hz, 2F, *p*), −165.0 (m, 4F, *m*) [$B(C_6F_5)_2$] [$\Delta\delta^{19}F_{m,p}$ = 7.1].

X-ray Crystal Structure Analysis of Compound 6a. Formula $C_{32}H_{11}B_2F_{15}P{\cdot}C_7H_8$, M = 814.32, colorless crystal, 0.33 × 0.26 × 0.22 mm, a = 11.1554(10) Å, b = 20.4812(14) Å, c = 15.9966(7) Å, β = 104.768(5)°, V = 3534.1(4) Å^3, ρ_{calc} = 1.530 g cm^{-3}, μ = 1.688 mm^{-1}, empirical absorption correction (0.605 ≤ T ≤ 0.707), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 25467 reflections collected (±h, ±k, ±l), (sin θ)/λ = 0.60 Å^{-1}, 6126 independent (R_{int} = 0.037) and 5493 observed reflections [$I > 2\sigma(I)$], 569 refined parameters, R1 = 0.039, wR2 = 0.103, max (min) residual electron density 0.30 (−0.20) e Å^{-3}. Hydrogen atoms calculated and refined as riding atoms.

Synthesis of Compound 6b. Di-*p*-tolylphosphanylethyne (92 mg, 0.40 mmol) and tris(pentafluorophenyl)borane (0.20 g, 0.40 mmol) were dissolved in toluene (4 mL) and stirred for 1 h at 80 °C until the solution turned brown. Then the reaction mixture was concentrated in vacuo and kept stirring at room temperature overnight until a white solid precipitated. The solid was collected by cannula filtration and dried in vacuo to give **5b** (52 mg, 35 μmol, 18%) as a white powder. Subsequently, the filtrate was irradiated by UV light (high-pressure mercury vapor lamp: HPK 125 W, Pyrex filter) for 3 h until the solution turned colorless. The solvent was removed in vacuo, and the residue crystallized from pentane to give **6b** as a white powder (60 mg, 80 μmol, 19%). Crystals of **6b** suitable for X-ray single crystal structure analysis were obtained by the slow diffusion of pentane into a saturated CH_2Cl_2 solution at −30 °C. Mp: 168 °C (dec). Elem anal. Calcd for $C_{34}H_{15}BF_{15}P$: C, 54.43; H, 2.02. Found: C, 54.62; H, 2.05. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ 7.29 (d, $^2J_{PH}$ = 12.9 Hz, 1H, =CH), 7.21 (m, 4H, *m*-tolyl), 7.18 (m, 4H, *o*-tolyl), 2.37 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (151 MHz): δ 170.2 (br, =CB), 143.3 (d, $^4J_{PC}$ = 2.5 Hz, *p*-tolyl), 132.0 (d, $^2J_{PC}$ = 9.8 Hz, *o*-tolyl), 130.2 (d, $^3J_{PC}$ = 11.2 Hz, *m*-tolyl), 126.5 (dm, $^1J_{PC}$ = 58.5 Hz, =CH), 122.4 (d, $^1J_{PC}$ = 48.0 Hz, *i*-tolyl), 21.7 (d, $^5J_{PC}$ = 1.4 Hz, CH_3) [C_6F_5 is not listed]. ^{11}B{^{1}H} NMR (192 MHz): δ = −4.7 ($\nu_{1/2} \approx$ 200 Hz). ^{31}P{^{1}H} NMR (243 MHz): δ = 12.0 ($\nu_{1/2} \approx$ 90 Hz). ^{19}F NMR (564 MHz): δ −131.3 (m, 4F, *o*), −158.2 (tm, $^3J_{FF}$ = 19.3 Hz, 2F, *p*), −165.2 (m, 4F, *m*) ($B(C_6F_5)_2$) [$\Delta\delta^{19}F_{m,p}$ = 7.0], −137.8 (m, 2F, *o*), −153.1 (t, $^3J_{FF}$ = 21.0 Hz, 1F, *p*), −163.6 (m, 2F, *m*) (C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 10.5].

X-ray Crystal Structure Analysis of Compound 6b. Formula $C_{34}H_{15}BF_{15}P$, M = 750.24, colorless crystal, 0.20 × 0.15 × 0.08 mm, a = 8.9861(1) Å, b = 12.7129(2) Å, c = 14.7045(1) Å, α = 71.570(6)°, β = 83.088(8)°, γ = 74.813(10)°, V = 1536.7(3) Å^3, ρ_{calc} = 1.621 g cm^{-3}, μ = 1.882 mm^{-1}, empirical absorption correction (0.704 ≤ T ≤ 0.864), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 20191 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 5217 independent (R_{int} = 0.059) and 4206 observed reflections [$I > 2\sigma(I)$], 462 refined parameters, R1 = 0.050, wR2 = 0.142, max (min) residual electron density 0.51 (−0.24) e Å^{-3}. Hydrogen atoms were calculated and refined as riding atoms.

Synthesis of Compound 11. Diphenylphosphanylethyne (0.11 g, 0.50 mmol) and methylbis(pentafluorophenyl)borane (0.18 g, 0.50 mmol) were dissolved in toluene (6.0 mL) and stirred for 5 h at 80 °C until the solution turned brown. Then the reaction mixture was kept at low temperature (−30 °C), and some colorless crystals precipitated. The crystals were collected by cannula filtration and dried in vacuo to give compound **11** (0.12 g, 0.11 mmol, 42%). Crystals of **11** suitable for X-ray single crystal structure analysis were obtained by keeping a saturated toluene solution at room temperature for 2 days. Mp: 244 °C. Elem anal. Calcd for $C_{54}H_{28}B_2F_{20}P_2$: C, 56.88; H, 2.47. Found: C, 56.73; H, 2.76. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ 7.84 (m, 4H, *o*-Ph^A), 7.81 (m, 2H, *p*-Ph^A), 7.71 (m, 2H, *p*-Ph^B), 7.67 (m, 4H, *o*-Ph^B), 7.64 (m, 4H, *m*-Ph^A), 7.56 (m, 4H, *m*-Ph^B), 7.31 (dd, $^3J_{PH}$ = 52.4 Hz, $^2J_{PH}$ = 29.0 Hz, 1H, =CH), 3.36 (1:1:1:1 q partially relaxed, $^1J_{BH} \approx$ 90 Hz, 1H, BH), 2.16 (s, 3H, CH_3), 0.00 (s, 3H, BCH_3). ^{13}C{^{1}H} NMR (151 MHz): δ 226.7 (br, =CB), 173.0 (br, BCP), 140.0 (d, $^2J_{PC}$ = 75.1 Hz, =CH), 135.3 (d, J = 3.1 Hz, *p*-Ph^A), 134.8 (d, J = 3.3 Hz, *p*-Ph^B), 133.60, 133.57 (each d, $^2J_{PC}$ = 11.5 Hz, *o*-Ph^{A,B}), 130.3 (d, $^3J_{PC}$ = 12.9 Hz, *m*-Ph^A), 130.0 (d, $^3J_{PC}$ = 13.6 Hz, *m*-Ph^B), 119.7 (dm, $^1J_{PC}$ = 91.3 Hz, *i*-Ph^B), 118.7 (dm, $^1J_{PC}$ = 83.1 Hz, *i*-Ph^A), 101.5 (dd, $^1J_{PC}$ = 95.5 and 67.0 Hz, PCP), 31.3 (br, CH_3), 10.5 (br, BCH_3) [C_6F_5 not listed]. ^{11}B NMR (192 MHz): δ −11.9 ($\nu_{1/2} \approx$ 100 Hz), −15.9 ($^1J_{BH} \approx$ 88 Hz). ^{31}P{^{1}H} NMR (243 MHz): δ 33.1 (dm, $^2J_{PP} \sim$ 158 Hz), 22.2 (dm, $^2J_{PP} \sim$ 158 Hz). ^{19}F NMR (564 MHz): δ −131.0, −131.5 (each m, each 2F, *o*-C_6F_5), −161.6 (t, $^3J_{FF}$ = 19.8 Hz), −161.7 (t, $^3J_{FF}$ = 21.0 Hz, each 1F, *p*-C_6F_5), −165.6, −165.7 (each m, each 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 4.0].

X-ray Crystal Structure Analysis of Compound 11. Formula $C_{54}H_{28}B_2F_{20}P_2{\cdot}2C_7H_8$, M = 1324.59, colorless crystal, 0.22 × 0.12 × 0.12 mm, a = 13.2776(4) Å, b = 13.9853(8) Å, c = 16.3101(9) Å, α = 93.485(3)°, β = 97.639(2)°, γ = 93.710(4)°, V = 2988.1(3) Å^3, ρ_{calc} = 1.472 g cm^{-3}, μ = 1.603 mm^{-1}, empirical absorption correction (0.719 ≤ T ≤ 0.830), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 45392 reflections collected (±h, ±k, ±l), (sin θ)/λ = 0.60 Å^{-1}, 10349 independent (R_{int} = 0.053) and 8413 observed reflections [$I > 2\sigma(I)$], 837 refined parameters, R1 = 0.055, wR2 = 0.153, max (min) residual electron density 0.50 (−0.35) e Å^{-3}. The hydrogen at the B1 atom was refined freely; others were calculated and refined as riding atoms.

Synthesis of Compound 12a. ***Caution!*** *Many isocyanides are toxic and must be handled with due care.* The combination of compound **5a** (29 mg, 20 μmol) with *n*-butyl isocyanide (1.7 mg, 20 μmol) in CH_2Cl_2 (1 mL) led instantaneously to a light-yellow solution. After the reaction mixture was stirred for 10 min, all volatiles were removed in vacuo and the obtained residue was washed with cold pentane (3 × 2 mL). The product (25 mg, 16.5 μmol, 83%) was obtained as light yellow powder. Crystals of **12a** suitable for X-ray single crystal structure analysis were obtained by the slow diffusion of pentane into a saturated CH_2Cl_2 solution at −30 °C. Mp: 215 °C (dec). Elem anal. Calcd for $C_{69}H_{31}B_2F_{30}NP_2$: C, 54.25; H, 2.05; N, 0.92. Found: C, 54.07; H, 1.96; N, 0.87. IR (KBr): $\tilde{\nu}$/cm^{-1} = 2308 (C≡N). ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ 8.02 (m, 2H, *o*-Ph^A), 7.97 (m, 2H, *o*-Ph^B), 7.78 (m, 1H, *p*-Ph^A), 7.72 (m, 4H, *o*-Ph^C), 7.70 (m, 4H, *m*-Ph^A), 7.67 (m, 1H, *p*-Ph^B), 7.61 (m, 1H, *p*-Ph^C), 7.50 (m, 4H, *m*-Ph^B), 7.49 (m, 4H, *m*-Ph^C), 7.39 (m, 1H, *p*-Ph^D), 7.20 (m, 2H, *o*-Ph^D), 7.14 (m, 2H, *m*-Ph^D), 6.80 (br dd, $^3J_{PH}$ = 55.8 Hz, $^2J_{PH}$ = 33.1 Hz, 1H, =CH), 4.73 (m, 1H, BCH), 2.84 (t, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2), 1.59 (m, 2H, CH_2), 1.30 (m, 2H, CH_2Me), 0.91 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (151 MHz): δ 162.1 (br, BCP), 140.8 (dm, $^1J_{PC}$ = 86.3 Hz, =CH), 135.2 (br, *o*-Ph^B), 133.60−133.38 (m, *o*,*p*-Ph^{A,C}, *p*-Ph^B), 131.9 (br d, $^2J_{PC}$ = 9.0 Hz, *o*-Ph^D), 131.6 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Ph^D), 130.0 (dm, $^1J_{PC}$ = 80.6 Hz, *i*-Ph^A), 129.7 (d, $^3J_{PC}$ = 11.7 Hz, *m*-Ph^A), 129.1 (d, $^3J_{PC}$ = 12.1 Hz, *m*-Ph^C), 128.5 (d, $^3J_{PC}$ = 12.0 Hz, *m*-Ph^B), 127.9 (d, $^1J_{PC}$ = 81.5 Hz, *i*-Ph^D), 127.7 (br, N≡C), 127.5 (d, $^3J_{PC}$ = 11.5 Hz, *m*-Ph^D), 126.0 (dd, $^1J_{PC}$ = 85.0 Hz, J = 3.6 Hz, *i*-Ph^C), 120.9 (d, $^1J_{PC}$ = 81.7 Hz, *i*-Ph^B), 44.7 (NCH_2), 29.4 (CH_2), 20.4 (br, BCH), 20.0

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(CH_2Me), 15.6 (dd, $^1J_{PC}$ = 117.9 and 89.5 Hz, PCP), 13.1 (CH_3) [C_6F_5 not listed]. $^{11}B\{^1H\}$ NMR (192 MHz): δ −13.5 ($\nu_{1/2} \approx 35$ Hz), −17.9 ($\nu_{1/2} \approx 200$ Hz). $^{31}P\{^1H\}$ NMR (243 MHz): δ 56.3 (dm, $^2J_{PP} \sim 150$ Hz), 22.3 (dm, $^2J_{PP} \sim 150$ Hz). ^{19}F NMR (470 MHz, 193 K, CD_2Cl_2): δ −121.6 (1F), −124.9 (1F), −129.9 (1F), −130.7 (1F), −131.4 (4F), −132.7 (1F), −133.3 (1F), −137.7 (1F), −141.9 (1F) (each m, *o*), −155.7 (1F), −156.6 (1F), −157.8 (1F), −160.4 (1F), −160.8 (1F), −161.2 (1F) (each m, each 1F, *p*), −159.9 (1F), −162.2 (1F), −162.4 (1F), −162.8 (1F), −162.9 (1F), −164.2 (2F), −164.4 (1F), −165.5 (1F), −165.8 (1F), −166.1 (1F), −166.4 (1F) (each m, *m*)(C_6F_5).

X-ray Crystal Structure Analysis of Compound 12a. Formula $C_{69}H_{31}B_2F_{30}NP_2$, M = 1527.51, colorless crystal, 0.28 × 0.08 × 0.03 mm, a = 13.7600(7) Å, b = 23.8790(20) Å, c = 21.9660(30) Å, β = 94.374(6)°, V = 7196.5(12) Å^3, ρ_{calc} = 1.410 g cm^{-3}, μ = 1.622 mm^{-1}, empirical absorption correction ($0.659 \leq T \leq 0.953$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 59373 reflections collected ($\pm h$, $\pm k$, $\pm l$), (sin θ)/λ = 0.60 Å^{-1}, 12072 independent (R_{int} = 0.011) and 6860 observed reflections [$I > 2\sigma(I)$], 938 refined parameters, R1 = 0.071, wR2 = 0.222, max (min) residual electron density 0.36 (−0.41) e Å^{-3}. Hydrogen atoms calculated and refined as riding atoms.

Synthesis of Compound 12b. ***Caution!*** *Many isocyanides are toxic and must be handled with due care.* The combination of compound **5b** (50 mg, 30 μmol) with *n*-butyl isocyanide (2.8 mg, 30 μmol) in CH_2Cl_2 (1 mL) led instantaneously to a light-yellow solution. After the reaction mixture was stirred for 10 min, the solvent was removed in vacuo and the obtained residue was washed with cold pentane (3 × 2 mL). The product (40 mg, 76%) was obtained as a light-yellow powder. Mp: 203 °C (dec). Elem anal. Calcd for $C_{73}H_{39}B_2F_{30}NP_2$: C, 55.37; H, 2.48; N, 0.88. Found: C, 55.22; H, 2.97; N, 0.78. IR (KBr): $\tilde{\nu}$/cm^{-1} = 2349 (C≡N). ^1H NMR (600 MHz, 299 K, CD_2Cl_2): δ 7.94 (m, 2H, *o*-tolyl^A), 7.87 (br m, 2H, *o*-tolyl^B), 7.56 (m, 2H, *o*-tolyl^C), 7.51 (m, *m*-tolyl^A), 7.30 (m, 2H, *m*-tolyl^B), 7.26 (m, 2H, *m*-tolyl^C), 7.01 (m, 2H, *o*-tolyl^D), 6.91 (m, *m*-tolyl^D), 6.70 (br dd, $^3J_{PH}$ = 54.3 Hz, $^2J_{PH}$ = 32.5 Hz, 1H, =CH), 4.73 (br m, 1H, BCH), 2.82 (m, 2H, NCH_2), 2.51 (s, $^{tolyl}CH_3{}^A$), 2.48 (s, $^{tolyl}CH_3{}^B$), 2.46 (s, $^{tolyl}CH_3{}^C$), 2.35 (s, $^{tolyl}CH_3{}^D$), 1.58 (m, 2H, CH_2), 1.29 (m, 2H, CH_2Me), 0.92 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (151 MHz): δ 161.8 (br, BCP), 144.82 (d, $^4J_{PC}$ = 3.1 Hz), 144.81 (d, $^4J_{PC}$ = 3.1 Hz, *p*-tolyl^{B,C}), 144.4 (d, $^4J_{PC}$ = 3.0 Hz, *p*-tolyl^A), 142.7 (d, $^4J_{PC}$ = 3.1 Hz, *p*-tolyl^D), 140.6 (dm, $^1J_{PC}$ = 86.9 Hz, =CH), 135.3 (br m, *o*-tolyl^B), 133.6 (t, J = 10.3 Hz, *o*-tolyl^A), 133.3 (d, $^2J_{PC}$ = 10.7 Hz, *o*-tolyl^C), 131.6 (br d, $^2J_{PC}$ = 8.3 Hz, *o*-tolyl^D), 130.4 (d, $^3J_{PC}$ = 12.2 Hz, *m*-tolyl^A), 129.6 (d, $^3J_{PC}$ = 12.4 Hz, *m*-tolyl^C), 129.2 (d, $^3J_{PC}$ = 12.4 Hz, *m*-tolyl^B), 128.0 (d, $^3J_{PC}$ = 11.8 Hz, *m*-tolyl^D), 127.9 (br, N≡C) [from the ghmbc experiment], 127.1 (dm, $^1J_{PC}$ = 82.3 Hz, *i*-tolyl^A), 125.3 (dm, $^1J_{PC}$ = 82.5 Hz, *i*-tolyl^D), 122.7 (dd, $^1J_{PC}$ = 87.2 Hz, $^3J_{PC}$ = 3.4 Hz, *i*-tolyl^C), 117.4 (dm, $^1J_{PC}$ = 81.8 Hz, *i*-tolyl^B), 44.5 (NCH_2), 29.4 (CH_2), 21.7 (d, J = 1.5 Hz, $^{tolyl}CH_3{}^A$), 21.6 (d, J = 1.3 Hz, $^{tolyl}CH_3{}^B$), 21.5 (br d, J = 1.0 Hz, $^{tolyl}CH_3{}^C$), 21.1 (d, J = 1.6 Hz, $^{tolyl}CH_3{}^D$), 20.5 (br, BCH), 20.0 (CH_2Me), 15.6 (dd, $^1J_{PC}$ = 119.7 and 90.9 Hz, PCP), 13.1 (CH_3) [C_6F_5 not listed]. $^{11}B\{^1H\}$ NMR (192 MHz): δ −13.6 ($\nu_{1/2} \approx 35$ Hz), −18.0 ($\nu_{1/2} \approx 250$ Hz). $^{31}P\{^1H\}$ NMR (243 MHz): δ 54.7 (d, $^2J_{PP} \sim 150$ Hz), 21.4 (d, $^2J_{PP} \sim 150$ Hz). ^{19}F NMR (470 MHz, 193 K): δ −121.2 (1F), −124.9 (1F), −129.9 (1F), −130.2 (1F), −131.2 (2F), −131.4 (1F), −131.5 (1F), −132.8 (1F), −133.1 (1F), −137.5 (1F), −142.2 (1F) (each m, *o*), −156.0, −157.2, −158.6, −161.0, −161.8, −161.8 (each 1F, each m, *p*), −161.5 (1F), −162.4 (1F), −162.5 (1F), −163.3 (1F), −163.5 (1F), −164.4 (3F), −166.0 (1F), −166.1 (1F), −166.6 (1F), −166.7 (1F) (each m, *m*)(C_6F_5).

■ ASSOCIATED CONTENT

Supporting Information

Text and figures giving further experimental and spectroscopic details and CIF files giving crystallographic data for **5b**, **6a**, **6b**, **11**, and **12a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[†]X-ray structure analyses.

Notes

The authors declare no competing financial interest.

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